DIPOLE MOMENTS OF PALMITIC ACID, ALEURITIC ACID AND ALKYL ESTERS OF ALEURITIC ACID

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ABSTRACT. Dipole moments of palmitic acid, aleuritic acid (9, 10, 16 trihydroxypalmitic acid) and methyl and ethyl esters of aleuritic acid have been determined from their dilute solutions in 1, 4 dioxane. The temperature of measurement was 25°C. for all but aleuritic acid for which the temperature 40°C. was used due to the latter's limited solubility in the above solvent at the lower temperature. The values obtained for palmitic acid, aleuritic acid, methyl aleuritate and ethyl aleuritate are 1.75, 4.28, 4.27 and 4.31 Debye units respectively. The cause of anomalous solubility of aleuritic acid or its esters in polar solvents or when some polar helper is added to the solvent has been discussed with reference to solvation and dissolution owing to the highly polar nature of these substances.

INTRODUCTION

Although the anomalous solubility of some natural resins in organic solvents was the subject of much speculation for a long time, no satisfactory explanation of the same came forth till very recently.[1] Some very interesting observations were made in this connection in that many of the non-solvents for such resins may be rendered good solvents for the same by the addition of small quantities of some 'polar-helpers' to these non-solvents. The effect of such polar-helpers has also been observed and recognised in many other fields.[2] The current conceptions[3] regarding solvation of large molecules and the consequent dissolution process may explain the rôle which these polar-helpers play in such non-solvents.

There are reasons to believe from what has been stated above that either the molecules of natural resins, such as shellac, pontianak or copal, are themselves polar in nature or the different constituent groups which make up such molecules behave as polar bodies towards different solvents, and consequent solvation and dissolution take place. It has been thought desirable, therefore, to study the dielectric properties of such resins and their constituent bodies in different solvents in order to throw light on the nature of their molecules from this point of view. The present paper only embodies the results of dipole measurement on aleuritic acid, the only acid isolated from shellac whose constitution has been definitely established[4] and the alkyl esters of this acid.

Since aleuritic acid is a hydroxy palmitic acid, it was also thought necessary to determine the dipole moment of palmitic acid from its dilute solutions in

dioxane as it is related to the above acid in structure. Its value in benzene although available[5,6] cannot be taken as its actual moment for single molecules owing to their association in that solvent. Wilson and Wenzke[7] have, however, shown that fatty acids have practically no complex solvent-solute interaction in 1, 4 dioxane and so their dipole moments determined from dilute solutions in the above solvent conform to the values of single molecules in the gaseous state. The evaluation of electric moment of palmitic acid from dioxane solutions was therefore undertaken, as no value of moment of this acid seemed to be available from this solvent. The limited solubility of aleuritic acid in dioxane also necessitated measurements on its methyl and ethyl esters, which are soluble in the above solvent.

PREPARATION OF MATERIALS

Dioxane.—American dioxane bottled by A. Boake Roberts & Co., Ltd., of England was allowed to stand over sodium wire for several days, distilled and the middle fraction boiling constantly at a fixed temperature collected. This fraction was further purified by refluxing over sodium for 8-10 hours and then again distilling. The main fraction distilling between 98°.0C. and 98°.1C. under 693 mm. of mercury* was collected by means of an efficient fractionating column. It was noticed that the sodium wires assumed the form of silver-white balls during refluxing and they retained their lustre in the liquid as reported by Eigenberger.[8]

$$F.P. = 11°.6C., \quad n^{25} = 1.4198, \quad d^{25} = 1.0282, \quad \epsilon^{25} = 2.2024$$

Benzene.—A sample of pure crystallisable benzene was dried over sodium wire for some days and refluxed over it for 8-10 hours. It was distilled and the main fraction boiling between 79°.5C. and 79°.6C. collected. This was then fractionally crystallised twice and the solid residue taken. This portion when molten was allowed to stand over fresh sodium wire which retained its lustre in the liquid. It was again fractionated by means of an efficient column and the main fraction used.

$$F.P. = 5°.5C., \quad n^{25} = 1.4985, \quad d^{25} = 0.8738, \quad \epsilon^{25} = 2.2725$$

Aleuritic acid.—The crude aleuritic acid, prepared from dewaxed lac according to the method of Nagel,[9] was freed from ether-soluble impurities by extraction with ether in a Soxhlet apparatus. This product was then refluxed with pure ethyl acetate and decolourising charcoal for six hours, filtered hot and then the solution allowed to crystallise. The first crop of crystals was separated from the mother-liquor and subsequently twice recrystallised from a mixture of alcohol and ethyl acetate. It was finally washed with pure and dry ether and dried in a vacuum oven. M. P. 99°.8C.

* The altitude of Namkum (Ranchi) being 2300 ft. above sea-level, its normal barometric height is about 700 mm

Methyl aleuritate.—A portion of the pure aleuritic acid thus obtained was refluxed with chemically pure methyl alcohol and a few c.cs. of pure concentrated sulphuric acid for 6 hours. The methyl ester was then obtained by precipitation from a large volume of water. This ester was dissolved in ether, the ethereal solution filtered and allowed to crystallise. These crystals were further purified by recrystallisation from dilute methyl alcohol and then dried in a vacuum-oven. M. P. 69°C.

Ethyl aleuritate.—Another portion of the pure aleuritic acid was similarly refluxed with absolute ethyl alcohol and a little of concentrated sulphuric acid for about 10 hours. The ethyl ester was obtained as before by precipitation from water. It was dissolved in ether, filtered and the solution allowed to crystallise. The final crystallisation was done from dilute ethyl alcohol, and the drying was carried in a vacuum-oven. M. P. 58°C.

Palmitic acid.—Merck's product was twice recrystallised from hot alcohol. M. P. 62.4°C

EXPERIMENTAL

Apparatus.—The substitution method of measurement was used employing General Radio type 516-C radio-frequency bridge[10] and a calibrated 1100 $\mu\mu$F General Radio variable air condenser. Another 25 $\mu\mu$F General Radio variable condenser having 1 $\mu\mu$F graduations was fitted with a precision slow-motion dial so that readings could be taken to 0.05 $\mu\mu$F. This was used in connection with the main condenser and the instrument calibrated in position. The oscillator employed was a General Radio Type 084-A modulated oscillator[11] which could give power over a wide range of frequency from 10 kilocycles to 30 megacycles. From this oscillator a current of 50-kilocycles modulated at 1000-cycles at about 15 volts was used for the bridge. The detector was a pair of high sensitivity headphones used in conjunction with a high gain amplifier specially built for this purpose. The sensitivity of the apparatus was very good and the frequency of 50-kilocycles was used in order to have the most sensitive arrangement in conjunction with the amplifier-detector.

The experimental cell was constructed of pyrex glass according to the design of Sayce and Briscoe and fully described by Le Fèvre.[12] The silvering of this cell was done according to the directions given by Sugden.[13] The cell could be placed inside a big thermos which served as a water thermostat. The temperature was kept constant within $0^{c}.05$C. The thermostat-water was earthed and the outer silver coating of the experimental cell was connected with the grounded terminal of the standard condenser. Screened cables were used for connecting the oscillator and the amplifier to the bridge, and the oscillator and the amplifier were kept at a distance from each other to avoid direct interference.

The apparatus was calibrated with pure and dry benzene and the capacity of the leads, etc., was found out from the 'zero capacity' of the experimental cell. This was obtained from the relation

$$C_0 = \frac{\epsilon . C_A - C_B}{\epsilon - 1}$$

where C_0 = 'zero capacity' of the cell,
C_A = air capacity of the same,
C_B = capacity of the cell filled with benzene,
and ϵ = dielectric constant of benzene.

With the value of C_0 thus obtained the dielectric constant of a solution or any other liquid was determined from

$$\epsilon_s = \frac{C_S - C_0}{C_A - C_0}$$

where C_S = the capacity of the cell when filled with the solution,
and ϵ_s = the dielectric constant of the solution.

The best condition of silence in the headphones was obtained by adjusting the power-factor knob of the radio frequency bridge in order that the headphones were actually connected to points which were not only at the same potential but also at the same phase.

Density measurements were carried out with a pyknometer of 25 c.c. capacity and the results may be considered to be accurate to 0.01%. Dielectric constant values are probably accurate to 0.03%.

Glass-stoppered Erlenmeyer flasks were used in making up solutions by weight. All measurements were made at 25°C. except for aleuritic acid for which the temperature 40°C. was used, since aleuritic acid was not sufficiently soluble in dry dioxane at 25°C. to permit accurate determination of its electric moment.

CALCULATIONS AND RESULTS

Polarisations were calculated using Sugden's formula[14] for specific polarisation in place of molar polarisation,

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{1}{d},$$

in which p is the specific polarisation, C, the dielectric constant, and d, the density of the liquid.

The total polarisation according to the above relation is

$$P_1 = M_1\left(P_2 + \frac{P_{12} - P_2}{w}\right)$$

in which P_{12} and P_2 are the specific polarisations of the mixture and the solvent respectively and w is the weight fraction of the solute of molecular weight M_1.

TABLE I

Dielectric constants, densities and polarisations. Solvent—Dioxane

Palmitic Acid (25°C.)				*Aleuritic Acid* (40°C.)				*Methyl aleuritate* (25°C.)				*Ethyl aleuritate* (25°C.)			
w	d	ϵ	P_1	w	d	ϵ	P_1	w	d	ϵ	P_1	w	d	ϵ	P_1
0.000000	1.0281	2.2024	—	0.000000	1.0112	2.1759	—	0.000000	1.0281	2.2024	—	0.000000	1.0281	2.2024	—
0.002121	1.0278	2.2052	140.0	0.002332	1.0112	2.1919	438.0	0.002252	1.0282	2.2186	463.3	0.002652	1.0281	2.2208	475.5
0.005033	1.0273	2.2094	142.4	0.002487	1.0113	2.1933	442.7	0.004258	1.0284	2.2346	479.6	0.004756	1.0283	2.2350	473.5
0.007605	1.0269	2.2129	141.6	0.004153	1.0113	2.2046	438.2	0.006750	1.0287	2.2654	476.2	0.007944	1.0285	2.2580	467.7
0.009479	1.0265	2.2151	140.4	0.004904	1.0114	2.2104	441.6	0.008850	1.0287	2.2668	456.3	0.014277	1.0291	2.3017	459.8
0.016231	1.0252	2.2248	142.3	0.006029	1.0114	2.2188	445.0	0.014500	1.0291	2.3056	448.0	0.020500	1.0294	2.3386	439.7
0.021806	1.0241	2.2330	143.5					0.020102	1.0295	2.3346	418.0				
0.027103	1.0229	2.2404	143.8												
0.032414	1.0218	2.2484	144.7												

TABLE II

Molar Refractions, Polarisations and Dipole Moments

Substance	MR_D	P_∞	$\mu \times 10^{18}$
Palmitic Acid	77.7	141.7	1.75
Aleuritic Acid	82.0	444.5	4.28
Methyl aleuritate	86.6	466.6	4.27
Ethyl aleuritate	91.2	478.4	4.31

Polarisations at infinite dilutions, P_∞, were calculated by means of equations suggested by Le Fèvre and Vine[15] involving specific polarisations and which are similar to Hedestrand's formula.[16] For the sake of comparison, the graphical extrapolation method suggested by Sugden[17] in extrapolating total polarisation—volume polarisability graph to the point $\epsilon=\epsilon_2$, where ϵ_2 is the dielectric constant of the solvent, was also used. The difference between the two P_∞ values obtained by these two methods was very small in the case of acids, but as the esters showed some difference, the graphical extrapolation method using P_1-w curves was employed for them.

Molar refractions were calculated as the sum of the atomic refractions[18] for the sodium D-line. The contributions of the atomic polarisations to polarisations at infinite dilutions were neglected. The dipole moments were calculated from the equations

$$\mu = 0.0127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T} \ ,$$

where T is the temperature of measurement in absolute scale.

DISCUSSIONS

The electric moment of palmitic acid in dilute benzene solutions has been found to be 0.72 Debye units by Smith[5] and 0.77D by Paranjpe and Deshpande.[6] Probably these values are for double molecules of the acid, since most of the fatty acids, especially the lower members of this group, are known to form double molecules in benzene due to association. Zahn[19] and Piekara[20] measured the moments of the first few members of the fatty acid group and found these moments to vary with temperature. They explained this variation as due to changing degree of association. Wilson and Wenzke,[7] however, found that the oxygenated solvent dioxane gave dipole moments of fatty acids quite in agreement with those determined by Zahn[21] for the gaseous state of their molecules, thus showing no effect of association. They gave the value 2.07D for formic acid and 1.74D for acetic acid, and observed that the lengthening of the carbon chain had practically no effect on the latter value of the moment. This they proved by obtaining the same value of moment for stearic acid, too, *viz.*, 1.74D. The value of the moment 1.75D for palmitic acid found here is therefore quite in agreement with their results and corroborates the above statement of these authors that the moment remains the same for all monobasic fatty acids after the first member of this group. This fact was also observed by Smith[5] independently from benzene solutions.*

It is generally believed from many observations of the type stated above that the electric doublet is located at the carboxylic head of these acid molecules, but unfortunately the moment assigned to the carboxyl group or the exact nature of the binding forces inside the group has not yet been finally settled. Williams[22] found this group to have a moment of 0.9×10^{-18} e.s. units, but

this value is usually considered to be too low considering the moments of single molecules of monobasic fatty acids in general. Eucken and Meyer[23] have calculated the limiting values of moment of the carboxyl group by considering the effect of rotation about the C-O bond in fatty acids and they gave 1.1D and 3.4D for its minimum and maximum values. The tendency of the acid hydrogen to be attracted towards the oxygen of the carboxyl would, according to these authors, accounts for moments of monobasic fatty acids to be nearer the minimum value of the carboxyl rather than the maximum. Very recently Brooks and Hobbs[24] have calculated from the observed moment of para-chlorobenzoic acid that the carboxyl makes an angle of 74° with the C-C line. But the calculated angle (from the accepted bond moments for C=O, C−O and O−H and assuming the valence angle at the oxygen atom to be 110° and that at the carbonation 125°) is 85°. The discrepancy is quite large and has been explained by them as due to resonance.

The constitution of aleuritic acid has been definitely established[4] as 9, 10, 16 trihydroxypalmitic acid. The structure may be written, therefore, as $CH_2OH.(CH_2)_5CHOH.CHOH(CH_2)_7.COOH$. The high value of moment can only be expected because the molecule contains three hydroxyl groups attached to the hydrocarbon chain of palmitic acid. It is useless, however, to try to calculate the dipole moment of aleuritic acid at the present state of our knowledge from the known bond moments of C=O, C−O and O−H, since rotation around the C−O bond brings in complexities and other unknown factors, such as induction and resonance, are also present.

The dipole moments of both the methyl and the ethyl esters of aleuritic acid are practically the same as that of the acid itself. From a knowledge of the moments of most of the fatty acid esters[25] this is to be expected.

It may now be understood that the highly polar nature of aleuritic acid or its esters may lead to the formation of solvates in polar solvents or when some polar helper is added to the solvent. It should be remembered, however, that polarity in itself cannot be the only criterion for solvation unless the substances differ in the character of their dipoles, *i.e.*, positive and negative, to have the affinity for the formation of solvates. For dissolution process it is recognised[26] now that polarity of the solvent is one of the most important factors for the organophillic compounds, such as cellulose, rubber, etc., probably because they contain heterogeneous polar groups, and the solvates present such a structure that they can then be easily dissolved by the solvent.

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